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# FIRST DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID AND RELATED pH VALUES OF PHTHALATE BUFFERS FROM 0° TO 60° C

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## ABSTRACT

Measurements were made at 5-degree intervals from 0° to 60° C of the potential difference between hydrogen electrodes and silver-silver-chloride electrodes in 45 aqueous solutions that contained various amounts of *o*-phthalic acid, acid potassium phthalate, and potassium chloride. The first dissociation constant of *o*-phthalic acid and related thermodynamic quantities were evaluated, and pH values were assigned to each of the 45 solutions.

The equation obtained for the first dissociation constant as a function of temperature is

$$\log K_1 = -561.57/T + 1.2843 - 0.0078833T,$$

where  $T = t^\circ\text{C} + 273.16$ .

The pH values of the solutions range from 2.70 to 3.26 and vary only slightly with changes in temperature. The solutions have good buffer capacity and may be readily prepared from pure materials. Each solution is suited for use as a pH standard.

The separation of the carboxyl groups in *o*-phthalic acid was found to be 1.66 Å by means of an equation relating this distance with the ratio of the two dissociation constants of *o*-phthalic acid. This value is higher than 1.53 Å obtained from X-ray measurements of the carbon-carbon distance in the diamond and 1.43 in the benzene molecule.

The problem of convergence or lack of convergence of apparent dissociation constants calculated by different methods to a single thermodynamic value in the limit of infinite dilution is discussed.

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## I. INTRODUCTION

A previous publication [1]<sup>1</sup> gave values of the second dissociation constant of *o*-phthalic acid, of related thermodynamic quantities,

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

and of the pH values of solutions containing acid potassium phthalate and dipotassium phthalate with or without potassium chloride at intervals of 5° from 0° to 60° C. There are now presented results of measurements over the same range of temperature of galvanic cells without liquid junction and comprised of hydrogen and silver-silver-chloride electrodes for the determination of the first dissociation constant of *o*-phthalic acid, of related thermodynamic quantities, and of the pH values of solutions containing acid potassium phthalate, *o*-phthalic acid, and potassium chloride. Both constants are needed for the calculation of the pH values of solutions of acid potassium phthalate by the equation

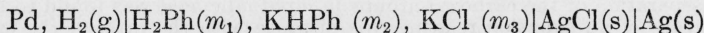
$$m_{\text{H}}^3 + [a + (K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}})]m_{\text{H}}^2 + [(K_1 K_2 f_{\text{H}_2\text{Ph}})/(f_{\text{H}}^2 f_{\text{Ph}})]m_{\text{H}} - (a K_1 K_2 f_{\text{H}_2\text{Ph}})/(f_{\text{H}}^2 f_{\text{Ph}}) = 0, \quad (1)$$

where  $K_1$  and  $K_2$  are, respectively, the first and second dissociation constants of *o*-phthalic acid,  $a$  is the stoichiometric concentration of acid potassium phthalate,  $m_{\text{H}}$  is the hydrogen-ion concentration, and  $f$  represents the activity coefficient of the species denoted by subscripts.<sup>2</sup>

## II. METHOD FOR THE DETERMINATION OF THE FIRST DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID

### 1. APPROXIMATE METHOD

In the determination of the first dissociation constant of *o*-phthalic acid by the electromotive-force method, measurements are made of the emf of the galvanic cell



for a series of solutions of different molalities,  $m_1$ ,  $m_2$ , and  $m_3$  and of various ratios,  $\text{H}_2\text{Ph}/\text{KHPh}$ , wherein the hydrogen and silver-silver-chloride electrodes are reversible, respectively, to hydrogen and chloride ions or their hydrates. The addition of the chloride is therefore a prerequisite for the use of silver-silver-chloride electrodes in such mixtures.

The calculation of the constant depends upon the equation

$$E = E^\circ - (RT/F) \ln (a_{\text{H}} a_{\text{Cl}}) = E^\circ - (RT/F) \ln a_{\text{H}} - (RT/F) \ln (f_{\text{Cl}} m_{\text{Cl}}), \quad (2)$$

which relates the emf of the cell,  $E$ , with the activities of the hydrogen and chloride ions, and upon the mass-action expression,

$$K_1 = (a_{\text{H}} a_{\text{HPh}})/(a_{\text{H}_2\text{Ph}}) = (a_{\text{H}} f_{\text{HPh}} m_{\text{HPh}})/(f_{\text{H}_2\text{Ph}} m_{\text{H}_2\text{Ph}}), \quad (3)$$

which defines the dynamic equilibrium between the ions and undissociated *o*-phthalic acid for the process  $\text{H}_2\text{Ph} \rightleftharpoons \text{H}^+ + \text{HPh}^-$ .  $E^\circ$  is the potential of the silver-silver-chloride electrode for unit activity of hydrochloric acid;  $a$ ,  $f$ , and  $m$  are the activity, activity coefficient, and molality of the species denoted by subscripts; and  $R$ ,  $T$ , and  $F$  have their usual significance.

<sup>2</sup> The symbols  $\text{H}_2\text{Ph}$ ,  $\text{HPh}$ , and  $\text{Ph}$  are used to designate, respectively, *o*-phthalic acid, acid phthalate ion, and diphtalate ion for convenience. The charges on the ions have been omitted.

In the above two equations,  $E$ ,  $E^\circ$ ,  $m_{\text{HPh}}$ ,  $m_{\text{H}_2\text{Ph}}$ ,  $m_{\text{Cl}}$ ,  $R$ ,  $T$ , and  $F$  are known quantities, whereas  $a_{\text{H}}$  and the other activities and activity coefficients are unknown quantities. The former unknown,  $(a_{\text{H}})$  may be eliminated by combination of eq 2 and 3, which gives

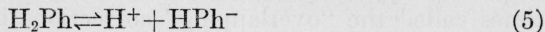
$$\{(E-E^\circ)/(2.3026RT/F) + \log (m_3m_1/m_2)\} + \log (f_{\text{Cl}}f_{\text{H}_2\text{Ph}}/f_{\text{HPh}}) = -\log K_1 = pK_1 \quad (4)$$

upon substitution of  $m_1$ ,  $m_2$ , and  $m_3$ , respectively, for  $\text{H}_2\text{Ph}$ ,  $\text{HPh}^-$ , and  $\text{Cl}^-$ . This equation still contains one unknown quantity—the third term on the left side, which is made up of the activity coefficients of one neutral molecule and two ions. The activity coefficient of the neutral molecule may be assigned a value of unity, as is customary. For example, Scatchard, Hamer, and Wood [2] by means of isotonic measurements obtained values of 1.0146, 0.9918, and 1.0026, respectively, for the activity coefficient of sucrose, urea, and glycerol of 0.1 molality. Extrapolation of their data gives values of 1.0029, 0.9984, and 1.0005 or an average value of 1.0006 for a 0.018-molal solution, the highest molality of *o*-phthalic acid used in this work. Hence, the assumption that the activity coefficient of undissociated *o*-phthalic acid is unity does not introduce an appreciable error in the final results. Even if the ions in solution do not conform to the laws of perfect solutes, the value of the third term should approach zero, as the values of the activity coefficients of the chloride and acid phthalate ions on a mole-fraction basis give the magnitude of the deviations of ions or molecules from the perfect state and should be practically equal. Only at infinite dilution do ions possess the characteristics of ideal solutes. Hence if values of the term in brackets, designated as  $pK_1$ , for decreasing values of  $(m_3m_1/m_2)$  are plotted against the ionic strength, values of  $pK_1$  are obtained by extrapolation to zero ionic strength.

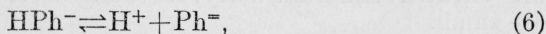
## 2. COMPLETE METHOD

In the foregoing it was assumed that the ratio,  $m_1/m_2$ , may be determined from the stoichiometrical molalities of *o*-phthalic acid and acid potassium phthalate. However, owing to various ionic equilibria, this is not strictly true and corrections must therefore be made.

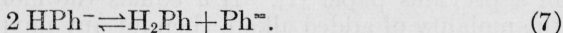
In a mixture of *o*-phthalic acid with its acid salt, the essential equilibria are



and



which upon subtraction give



In each case, the ions and molecules are in dynamic equilibrium defined by the mass-action expressions. These give, respectively, for processes 6 and 7

$$K_2 = (a_{\text{H}}a_{\text{Ph}})/a_{\text{HPh}} = (a_{\text{H}}f_{\text{Ph}}m_{\text{Ph}})/(f_{\text{HPh}}m_{\text{HPh}}) \quad (8)$$

and

$$K_2/K_1 = (a_{\text{Ph}}a_{\text{H}_2\text{Ph}})/a_{\text{HPh}}^2 = (f_{\text{Ph}}f_{\text{H}_2\text{Ph}}m_{\text{Ph}}m_{\text{H}_2\text{Ph}})/(f_{\text{HPh}}m_{\text{HPh}})^2. \quad (9)$$

The expression for process 5 is given by eq 3, where the terms have the same significance as given above.

As a result of these equilibria, eq 10 applies to a solution composed of  $\text{H}_2\text{Ph}$  of molality of  $m_1$  and of  $\text{KHPH}$  of a molality of  $m_2$

$$m_{\text{H}_2\text{Ph}} = m_1 - m_{\text{H}} + m_{\text{Ph}} \quad (10)$$

as  $\text{H}_2\text{Ph}$  is removed to form hydrogen ions in reaction 5 and is formed in reaction 7 in an amount equivalent to  $\text{Ph}^-$ . Furthermore, eq 11 holds

$$m_{\text{HPh}} = m_2 + m_{\text{H}} - 2m_{\text{Ph}} \quad (11)$$

as  $\text{HPh}^-$  is formed in reaction 5 and removed in reaction 7 in amounts equivalent, respectively, to  $\text{H}^+$  and  $2\text{Ph}^-$ . Consequently, the stoichiometrical molalities of  $\text{H}_2\text{Ph}$  and  $\text{KHPH}$  will be altered,<sup>3</sup> and a solution containing them will also contain a quantity of  $\text{Ph}^-$  ions. However, if  $K_2/K_1$  is less than about  $10^{-3}$  the tendency of reaction 7 to take place from left to right will be small and  $m_{\text{Ph}}$  in eq 10 and 11 may be neglected, leaving only corrections for  $m_{\text{H}}$ .

The values of  $m_{\text{H}}$  may be obtained from the emf of the cell as follows [3]: Rearrangement of eq 2 gives

$$(E - E^\circ)/(2.3026RT/F) + \log m_{\text{Cl}} + \log f_{\text{H}}f_{\text{Cl}} = -\log m_{\text{H}}. \quad (12)$$

Values of  $\log f_{\text{H}}f_{\text{Cl}}$  may be obtained by either (1) the limiting law of Debye and Hückel [4],  $-\log f_{\text{H}}f_{\text{Cl}} = 2A\sqrt{\mu}$ ; (2) the Guggenheim equation [5],  $-\log f_{\text{H}}f_{\text{Cl}} = 2A\sqrt{\mu}/(1 + \sqrt{\mu})$ ; (3) the extended Debye-Hückel equation [4]  $-\log f_{\text{H}}f_{\text{Cl}} = 2A\sqrt{\mu}/(1 + Ba_1\sqrt{\mu})$ ; or by (4) the Hückel extension of the Debye-Hückel equation [6],  $-\log f_{\text{H}}f_{\text{Cl}} = 2A\sqrt{\mu}/(1 + Ba_1\sqrt{\mu}) + \beta\mu$ . Thus four different values of  $m_{\text{H}}$  may be obtained, depending upon which equation is used to evaluate  $-\log f_{\text{H}}f_{\text{Cl}}$ . The four values of  $m_{\text{H}}$  agree more closely for dilute solutions, as the four expressions for the activity coefficient become equivalent at extreme dilutions. As  $\mu = m_2 + m_3 + m_{\text{H}}$  each calculation involves a successive approximation. First,  $\mu$  is taken equal to  $m_2 + m_3$ , and a provisional value of  $m_{\text{H}}$  is calculated by eq 12 and one of the Hückel equations. With this value of  $m_{\text{H}}$  a new  $\mu$  is determined from the relation  $\mu = m_2 + m_3 + m_{\text{H}}$ , and so on until self-consistent values of  $\mu$  and  $m_{\text{H}}$  are obtained.<sup>4</sup>

From data reported in the literature [7] for *o*-phthalic acid,  $K_2/K_1$  is about  $3 \times 10^{-3}$ , which exceeds the condition postulated for the neglect of  $m_{\text{Ph}}$  in eqs 10 and 11. Therefore, corrections for  $\text{Ph}^-$ , sometimes called the "overlapping" corrections because  $\text{H}_2\text{Ph}$  and  $\text{HPh}^-$  are titrated simultaneously, become necessary, even though they are small.

The corrections may be obtained as follows by methods described in a previous paper [1]. If  $a$  equals the molality of the acid and  $b$  the molality of added alkali, then for any mixture of the two

$$a = m_{\text{H}_2\text{Ph}} + m_{\text{HPh}} + m_{\text{Ph}}, \quad (13)$$

$$b + m_{\text{H}} = m_{\text{HPh}} + 2m_{\text{Ph}}. \quad (14)$$

<sup>3</sup> The concentrations of  $\text{H}_2\text{Ph}$  may be determined directly by partition methods if proper standard states are chosen for each solvent. For a determination of the concentration of undissociated molecules by the spectrophotometric method, see reference [26].

<sup>4</sup> This successive approximation involves the use of two equations, eq 12 and the equation  $\mu = m_2 + m_3 + m_{\text{H}}$ . Actually,  $\mu = m_2 + m_3 + m_{\text{H}} - m_{\text{Ph}}$ , where values of  $m_{\text{Ph}}$  are given by eq 15. Complete calculations of  $\mu$  therefore involves successive approximations by using three equations (see complete treatment).



By the use of these equations and eq 3 and 8, eq 15,

$$m_{\text{Ph}} = \frac{[(K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}}) + m_{\text{H}}](b + m_{\text{H}}) - (a K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}})}{2m_{\text{H}} + (K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}})}, \quad (15)$$

results if eq 16,

$$m_{\text{H}}^3 + [a + (K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}})]m_{\text{H}}^2 + [(K_1 K_2 f_{\text{H}_2\text{Ph}})/(f_{\text{H}}^2 f_{\text{Ph}}) + (b K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}}) - (a K_1 f_{\text{H}_2\text{Ph}})/(f_{\text{H}} f_{\text{HPh}})]m_{\text{H}} + [(K_1 K_2 f_{\text{H}_2\text{Ph}})/(f_{\text{H}}^2 f_{\text{Ph}})](b - 2a) = 0, \quad (16)$$

obtained by the elimination of  $m_{\text{H}_2\text{Ph}}$ ,  $m_{\text{HPh}}$ , and  $m_{\text{Ph}}$  in eq 3, 8, 10, and 11, is satisfied for the solutions of any composition and concentration. However, solution of eq 15 requires a knowledge of  $m_{\text{H}}$ , the activity coefficients,  $K_1$ , and  $K_2$ . Values of  $m_{\text{H}}$  are obtained by eq 12 discussed above. Values of the activity coefficients are obtained by the Debye-Hückel equations given above. Values of  $K_2$  are taken from a previous publication by Hamer and Acree [1]. Values of  $K_1$  used first are those obtained by the simplified procedure described above. After values of  $m_{\text{Ph}}$  are calculated in this way, they are used in eq 10 and 11 to calculate new values of the molality of  $\text{H}_2\text{Ph}$  and  $\text{HPh}^-$ . These latter values are then used to calculate new values of  $\mu$  and  $K_1$ , and the arithmetical procedure is continued until self-consistent values of  $K_1$ ,  $\mu$ , and  $m_{\text{Ph}}$  are obtained (see footnote 4 for calculations of values of ionic strength). The final values of  $pK_1$  are then obtained by the equation

$$(E - E^\circ)/(2.3026RT/F) + \log [m_3(m_1 - m_{\text{H}} + m_{\text{Ph}})/(m_2 + m_{\text{H}} - 2m_{\text{Ph}})] + \log (f_{\text{Cl}}/f_{\text{HPh}}) = -\log K_1 = pK_1, \quad (17)$$

where the same Debye-Hückel expression is used for the term  $\log (f_{\text{Cl}}/f_{\text{HPh}})$  as was employed to calculate values of  $m_{\text{H}}$  and  $m_{\text{Ph}}$ .

### III. EXPERIMENTAL PROCEDURES

#### 1. MATERIALS AND SOLUTIONS

The solutions used in this investigation were prepared in a  $\text{CO}_2$ -free atmosphere from known weights of stock solutions containing *o*-phthalic acid, acid potassium phthalate, and potassium chloride by dilution with known weights of conductivity water having a specific conductance of 0.6 to  $1.0 \times 10^{-6}$  mho. Two different stock solutions were used. The stock solutions for series I, II, III, and IV were prepared from known weights of dry *o*-phthalic acid, dry acid potassium phthalate, dry potassium chloride, and conductivity water. The stock solution for series V was prepared by the addition of the requisite amount of dry acid potassium phthalate to a standardized solution of hydrochloric acid.

Solutions containing more than 0.018 mole of *o*-phthalic acid and acid potassium phthalate were not used, as crystals of phthalic acid separate from more concentrated solutions at the lower temperatures. After the solutions were prepared, they were deaerated by means of hydrogen gas, and corrections were made for loss of water from the solutions and the differences between the densities of hydrogen and air.

Resublimed phthalic anhydride that gave less than 0.002-percent ash when ignited was boiled with distilled water. The resulting *o*-

phthalic acid was then recrystallized three times from distilled water and extracted with benzene in a Soxhlet extractor. After distillation of the benzene, the acid was boiled with water to remove any traces of anhydride that may have been formed and was finally recrystallized from water. After air-drying, the crystals were lightly ground in an agate mortar and dried in vacuum at room temperature over anhydrous magnesium perchlorate. Two lots of the acid were prepared and the purity of each was tested by weight titration in  $\text{CO}_2$ -free atmosphere against  $\text{CO}_2$ -free sodium hydroxide standardized against acid potassium phthalate, National Bureau of Standards Standard Sample 84a, phenolphthalein solution, being used as the indicator. The purity of one lot of the acid as indicated by the titrations was 100 percent and that of the other was 99.85 percent. However, when samples of the second lot were carefully ground for a second time and redried in vacuum at room temperature over anhydrous magnesium perchlorate the purity rose to 100 percent. Hence, it was assumed that the impurity was water entrapped in the crystals, and allowance was made for it in the preparation of the solutions.

The acid potassium phthalate was NBS Standard Sample 84a having a certified purity of 100.00 percent determined by titration. It was dried according to the directions given in the Bureau certificate and was allowed to cool in a desiccator, concentrated sulfuric acid being used as the desiccant.

The potassium chloride was recrystallized twice from conductivity water and then thrice from 95-percent ethanol to remove the last traces of bromide. It was dried for 10 hours at  $110^\circ\text{C}$  and allowed to cool in a desiccator over concentrated sulfuric acid.

The hydrochloric acid solution was prepared by dissolving in conductivity water the hydrogen chloride gas formed by the action of concentrated sulfuric acid on lumps of fused ammonium chloride. The strength of the acid was determined by weight titration with a solution of carbonate-free sodium hydroxide standardized against acid potassium phthalate, NBS Standard Sample 84a. Phenolphthalein solution was used as the indicator in each case. Determinations agreed within 0.04 percent.

## 2. ELECTRODES AND APPARATUS

Hydrogen electrodes of platinum foil covered with palladium were prepared as described in another paper [10]. Electrodes of this type do not catalyze the reduction of phthalates, and they function reversibly for well over 100 hours.

Silver-silver-chloride electrodes of the thermal-electrolytic type were prepared from pure materials by the method previously described [9]. They were aged sufficiently to bring them to a stable state [10, 11].

The details of the apparatus employed in these studies, including the cells, bubble tubes, thermostat, and the emf recording instruments have been described by Hamer and Acree [9]. The cells and bubble tubes were filled under reduced pressure, the temperature of the thermostat was controlled within  $0.01^\circ\text{C}$  at all the temperatures, and the emf was measured by means of a calibrated potentiometer with galvanometer and standard cell. The emf measurements were corrected in the usual manner to 1 atmosphere of hydrogen pressure.

IV. CALCULATION OF THE FIRST DISSOCIATION CONSTANT OF *o*-PHTHALIC ACID

The electromotive forces obtained at intervals of 5 degrees from 0° to 60° C in the five series of experiments on different ratios,  $H_2Ph/KHPh$ , and different chloride ratios,  $KCl/KHPh$ , designated as series I to V, are given in tables 1 to 5. The compositions of the different solutions are defined in terms of the molality of acid potassium phthalate given in column 1 (tables 3 and 4 excepted) and the buffer ratio given at the top of each table. In series I to V the solutions had a buffer ratio, respectively, of 1.5, 2.0, 1.0, 2.0, and 1.5 and a  $KCl/KHPh$  ratio, respectively, of 1.0, 1.0, variable ratio, variable ratio, and 1.5. In series I, four measurements marked by a superscript *a* were for a buffer ratio of 1.5063 and a  $KCl/KHPh$  ratio of unity.

TABLE 1.—*Electromotive forces of galvanic cells with hydrogen and silver-silver chloride electrodes and containing mixtures of phthalates and chlorides*

SERIES 1 <sup>a</sup> [MOLALITY OF <i>o</i> -PHTHALIC ACID=1.5×MOLALITY OF ACID POTASSIUM PHTHALATE, MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE]							
Solution number	Molality of $KHPh$	Temperature in degrees centigrade					
		0	5	10	15	20	25
	<i>Moles of solute per 1,000 g of water</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>
I 1.....	0.0018357	0.55244	0.55577	0.55904	0.56217	0.56519	0.56812
I 2.....	.0019071	.55119	.55444	.55771	.56076	.56382	.56672
I 3.....	.0027658	.53897	.54204	.54516	.54794	.55080	.55352
I 4.....	.0034165	.53218	.53520	.53813	.54090	.54359	.54626
I 5.....	.0039521	.52765	.53062	.53348	.53600	.53880	.54131
I 6.....	<sup>a</sup> .0040518	.52681	.52979	.53258	.53523	.53784	.54026
I 7.....	.0046056	.52299	.52589	.52871	.53121	.53372	.53619
I 8.....	.0047953	.52182	.52455	.52734	.52993	.53244	.53493
I 9.....	.0068606	.51109	.51378	.51631	.51869	.52105	.52332
I 10.....	.0079547	.50686	.50935	.51196	.51418	.51645	.51868
I 11.....	.0081020	.50628	.50888	.51134	.51361	.51591	.51807
I 12.....	<sup>a</sup> .011058	.49738	.49981	.50211	.50426	.50637	.50841
I 13.....	<sup>a</sup> .011799	.49558	.49800	.50025	.50238	.50445	.50644
I 14.....	<sup>a</sup> .011913	.49533	.49772	.49995	.50207	.50418	.50612
I 15.....	.012000	.49522	.49760	.49983	.50194	.50401	.50606

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>
I 1.....	0.57102	0.57362	0.57620	0.57857	0.58103	0.58337	0.58563
I 2.....	.56949	.57213	.57474	.57709	.57942	.58179	.58392
I 3.....	.55613	.55857	.56098	.56309	.56529	.56749	.56956
I 4.....	.54876	.55108	.55339	.55540	.55751	.55965	.56154
I 5.....	.54373	.54605	.54828	.55020	.55222	.55428	.55618
I 6.....	.54279	.54501	.54728	.54917	.55126	.55329	.55514
I 7.....	.53852	.54081	.54287	.54488	.54678	.54873	.55059
I 8.....	.53724	.53939	.54153	.54342	.54536	.54738	.54920
I 9.....	.52544	.52752	.52942	.53123	.53297	.53481	.53650
I 10.....	.52077	.52272	.52457	.52627	.52805	.52979	.53142
I 11.....	.52018	.52212	.52399	.52568	.52735	.52918	.53077
I 12.....	.51038	.51216	.51388	.51544	.51704	.51866	.52015
I 13.....	.50839	.51019	.51182	.51343	.51496	.51655	.51798
I 14.....	.50806	.50989	.51155	.51309	.51458	.51619	.51763
I 15.....	.50800	.50971	.51142	.51292	.51447	.51606	.51750

<sup>a</sup> Molality of *o*-phthalic acid=1.5063×molality of acid potassium phthalate and molality of potassium chloride=molality of acid potassium phthalate.

TABLE 2.—*Electromotive forces of galvanic cells with hydrogen and silver-silver-chloride electrodes and containing mixtures of phthalates and chlorides*

SERIES II. $\left\{ \begin{array}{l} \text{MOLALITY OF O-PHTHALIC ACID} = 2.0000 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{array} \right.$							
Solution number	Molality of KHPH	Temperature in degrees centigrade					
		0	5	10	15	20	25
	<i>Moles of solute per 1,000 g of water</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>
II 1.....	0.0008187	0.57528	0.57902	0.58207	0.58616	0.58954	0.59284
II 2.....	.0014005	.55627	.55976	.56299	.56618	.56920	.57227
II 3.....	.0014548	.55492	.55837	.56166	.56479	.56784	.57085
II 4.....	.0023517	.53888	.54194	.54504	.54783	.55061	.55334
II 5.....	.0024641	.53721	.54037	.54336	.54622	.54900	.55170
II 6.....	.0031025	.52996	.53279	.53571	.53839	.54105	.54359
II 7.....	.0036743	.52441	.52738	.53011	.53273	.53531	.53779
II 8.....	.0050000	.51490	.51763	.52025	.52272	.52513	.52745
II 9.....	.0071782	.50413	.50661	.50901	.51130	.51347	.51565
II 10.....	.0090000	.49750	.49993	.50219	.50437	.50645	.50847

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>
II 1.....	0.59608	0.59897	0.60196	0.60405	0.60739	0.61004	0.61278
II 2.....	.57515	.57770	.58047	.58284	.58530	.58775	.59005
II 3.....	.57382	.57628	.57871	.58133	.58375	.58619	.58853
II 4.....	.55590	.55832	.56070	.56285	.56499	.56715	.56900
II 5.....	.55418	.55658	.55896	.56105	.56323	.56538	.56739
II 6.....	.54596	.54829	.55053	.55258	.55451	.55654	.55841
II 7.....	.54006	.54225	.54449	.54639	.54833	.55025	.55208
II 8.....	.52962	.53180	.53365	.53545	.53718	.53906	.54082
II 9.....	.51768	.51959	.52139	.52302	.52462	.52627	.52783
II 10.....	.51044	.51237	.51394	.51539	.51699	.51852	.51999

TABLE 3.—*Electromotive forces of galvanic cells with hydrogen and silver-silver-chloride electrodes and containing mixtures of phthalates and chlorides*

SERIES III. MOLALITY OF O-PHTHALIC ACID=MOLALITY OF ACID POTASSIUM PHTHALATE=0.018							
Solution number	Molality of KCl	Temperature in degrees centigrade					
		0	5	10	15	20	25
	<i>Moles of solute per 1,000 g of water</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>
III 1.....	0.005	0.52279	0.52569	0.52850	0.53116	0.53375	0.53630
III 2.....	.0079994	.51179	.51446	.51708	.51954	.52193	.52433
III 3.....	.010	.50655	.50917	.51166	.51402	.51632	.51856
III 4.....	.014	.49867	.50109	.50352	.50573	.50788	.51005
III 5.....	.018	.49282	.49516	.49744	.49951	.50154	.50354

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>	<i>v</i>
III 1.....	0.53873	0.54098	0.54327	0.54534	0.54739	0.54957	0.55153
III 2.....	.52649	.52859	.53064	.53249	.53441	.53629	.53812
III 3.....	.52070	.52264	.52465	.52638	.52823	.53002	.53184
III 4.....	.51197	.51380	.51563	.51718	.51898	.52059	.52215
III 5.....	.50541	.50717	.50891	.51039	.51196	.51360	.51496



TABLE 4.—*Electromotive forces of galvanic cells with hydrogen and silver-silver-chloride electrodes and containing mixtures of phthalates and chlorides*

		SERIES IV. $\begin{cases} \text{MOLALITY OF } o\text{-PHTHALIC ACID} = 0.018. \\ \text{MOLALITY OF ACID POTASSIUM PHTHALATE} = 0.009. \end{cases}$					
Solution number	Molality of KCl	Temperature in degrees centigrade					
		0	5	10	15	20	25
	<i>Moles of solute per 1,000 g of water</i>						
IV 1.....	0.003	0.52310	0.52607	0.52877	0.53135	0.53394	0.53647
IV 2.....	.005	.51119	.51385	.51639	.51876	.52117	.52337
IV 3.....	.006985	.50340	.50589	.50833	.51155	.51280	.51491
IV 4.....	.009	.49749	.49987	.50223	.50433	.50642	.50846
IV 5.....	.049305	.45838	.46008	.46170	.46315	.46455	.46582

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
IV 1.....	<i>v</i> 0.53884	<i>v</i> 0.54110	<i>v</i> 0.54323	<i>v</i> 0.54526	<i>v</i> 0.54727	<i>v</i> 0.54939	<i>v</i> 0.55127
IV 2.....	.52558	.52713	.52960	.53133	.53317	.53500	.53664
IV 3.....	.51693	.51885	.52066	.52226	.52394	.52564	.52718
IV 4.....	.51037	.51218	.51391	.51538	.51697	.51852	.52000
IV 5.....	.46702	.46800	.46907	.46985	.47066	.47146	.47217

TABLE 5.—*Electromotive forces of galvanic cells with hydrogen and silver-silver-chloride electrodes and containing mixtures of phthalates and chlorides.*

		SERIES V. $\begin{cases} \text{MOLALITY OF } o\text{-PHTHALIC ACID} = 1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = 1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{cases}$					
Solution number	Molality of KHPH	Temperature in degrees centigrade					
		0	5	10	15	20	25
	<i>Moles of solute per 1,000 g of water</i>						
V 1.....	0.0009423	0.56610	0.56970	0.57319	0.57648	0.57974	0.58876
V 2.....	.0016280	.54703	.55030	.55343	.55641	.55938	.56215
V 3.....	.0026071	.53145	.53440	.53728	.54009	.54269	.54537
V 4.....	.0030788	.52614	.52906	.53188	.53453	.53704	.53957
V 5.....	.0036444	.52077	.52358	.52631	.52887	.53143	.53371
V 6.....	.0038552	.51909	.52185	.52456	.52710	.52947	.53182
V 7.....	.0041264	.51697	.51975	.52237	.52486	.52730	.52956
V 8.....	.0044082	.51489	.51757	.52021	.52271	.52503	.52741
V 9.....	.0054960	.50820	.51091	.51342	.51573	.51795	.52023
V 10.....	.0056467	.50740	.51010	.51255	.51486	.51711	.51931

Solution number	Temperature in degrees centigrade						
	30	35	40	45	50	55	60
V 1.....	<i>v</i> 0.59198	<i>v</i> 0.59486	<i>v</i> 0.59157	<i>v</i> 0.59408	<i>v</i> 0.59665	<i>v</i> 0.59924	<i>v</i> 0.60162
V 2.....	.56488	.56751	.56998	.57210	.57450	.57680	.57894
V 3.....	.54777	.55002	.55228	.55437	.55618	.55846	.56037
V 4.....	.54188	.54417	.54626	.54826	.55015	.55220	.55412
V 5.....	.53604	.53829	.54033	.54216	.54407	.54603	.54776
V 6.....	.53419	.53629	.53829	.54015	.54196	.54389	.54558
V 7.....	.53185	.53392	.53592	.53774	.53958	.54142	.54314
V 8.....	.52955	.53164	.53364	.53544	.53717	.53903	.54071
V 9.....	.52229	.52423	.52616	.52777	.52954	.53127	.53284
V 10.....	.52134	.52322	.52516	.52676	.52849	.53027	.53183

The hydrogen-ion concentration for each solution was calculated by eq 12 and by the use of the data for  $E^\circ$  determined by Harned and Ehlers [12], the values of  $R$ ,  $T$ , and  $F$  given by Hamer, Burton, and Acree [13], and (1) the limiting law of Debye and Hückel; (2) the Guggenheim expression; (3) the extended equation of Debye and Hückel, in which  $a_i$  was taken equal to 3.76 Å for each temperature; and (4) the Hückel extension of the Debye-Hückel equation in which  $a_i$  was taken equal to 3.76 Å and the  $\beta$  term was calculated from the values of  $\beta$  of the various ions given in another paper [1]. Method (4) is subsequently designated as the complete method. The value of 3.76 Å for  $a_i$  was reported in another paper [1] on the determination of the second dissociation constant of *o*-phthalic acid. It is to be expected that the same value of  $a_i$  should apply to the complete system of *o*-phthalic acid and potassium hydroxide regardless of the pH values. For example, Harned, Morrison, Walker, Donelson, and Calmon [14] found that the value of  $a_i$  for hydrochloric acid at 25° C did not change significantly in going from pure water with dielectric constant of 78.54 to a 82-percent dioxane-water mixture of dielectric constant of 10. As the dielectric constants of solutions suitable for the determination of  $K_1$  and  $K_2$  for *o*-phthalic acid should be nearly the same, it is to be expected that the same  $a_i$  value should apply. The values of  $\beta_{Cl}$ ,  $\beta_{HPh}$ , and  $\beta_{Ph}$  for use with the respective concentrations of the ions were taken from another paper on the determination of the second dissociation constant of *o*-phthalic acid, and  $\beta_H$  is taken equal to  $\beta_{Cl}$ <sup>5</sup>.

The four different sets of  $m_H$  values were then used in eqs. 10 and 11 to calculate values of  $m_{H_2Ph}$  and  $m_{HPh}$ , which were used in eq 17 to calculate values of  $pK'_1$ . In this calculation  $m_{Ph}$  was taken equal to zero. Values of  $pK'_1$  calculated in this manner for a temperature of 25° C are given in table 6 in the columns labeled "without overlapping corrections".

TABLE 6.—Summary of  $pK'_1$  values at 25° C for *o*-phthalic acid obtained by different methods of calculation

SERIES I. $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHthalic ACID} = 1.5 \times \text{MOLALITY OF ACID POTASSIUM PHthalate.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = \text{MOLALITY OF ACID POTASSIUM PHthalate.} \end{array} \right.$								
Molality of acid potassium phthalate	$pK'_1$ (without overlapping corrections) <sup>a</sup>				$pK'_1$ (with overlapping corrections) <sup>b</sup>			
	Limiting law of Debye and Hückel	Guggenheim	3.76 Å	3.76 Å and $\beta$	Limiting law of Debye and Hückel	Guggenheim	3.76 Å	3.76 Å and $\beta$
0.0018357.....	2.9369	2.9405	2.9412	2.9417	2.9477	2.9487	2.9494	2.9496
.0019071.....	2.9365	2.9402	2.9409	2.9414	2.9482	2.9493	2.9490	2.9492
.0027658.....	2.9376	2.9417	2.9426	2.9432	2.9471	2.9477	2.9495	2.9498
.0034165.....	2.9384	2.9427	2.9434	2.9440	2.9472	2.9492	2.9501	2.9504
.0039521.....	2.9378	2.9422	2.9430	2.9436	2.9482	2.9485	2.9494	2.9497
.0040518.....	2.9368	2.9391	2.9409	2.9435	2.9481	2.9484	2.9493	2.9496
.0046056.....	2.9372	2.9418	2.9426	2.9432	2.9484	2.9489	2.9488	2.9492
.0047953.....	2.9389	2.9436	2.9440	2.9450	2.9470	2.9495	2.9504	2.9508
.0068606.....	2.9377	2.9428	2.9436	2.9443	2.9452	2.9482	2.9493	2.9497
.0079547.....	2.9380	2.9433	2.9442	2.9449	2.9433	2.9485	2.9496	2.9500
.0081020.....	2.9372	2.9425	2.9433	2.9441	2.9445	2.9477	2.9488	2.9492
.011058.....	2.9369	2.9427	2.9439	2.9447	2.9430	2.9476	2.9487	2.9496
.011799.....	2.9366	2.9424	2.9433	2.9441	2.9439	2.9477	2.9488	2.9491
.011913.....	2.9360	2.9418	2.9427	2.9435	2.9432	2.9467	2.9478	2.9483
.012000.....	2.9373	2.9431	2.9440	2.9448	2.9446	2.9482	2.9493	2.9498

See footnotes at end of table.

<sup>5</sup> It is well known that the activity coefficient of an ion cannot be determined experimentally without some assumption. In this paper the assumption is made that the activity coefficients of ions are given by the Hückel equation and that the "salting-out" terms of the chloride and hydrogen ions are equal. For more details regarding assumptions in pH determinations, see references [9, 13, 15, and 16].

TABLE 6.—Summary of  $pK'_1$  values at 25° C for *o*-phthalic acid obtained by different methods of calculation—Continued

SERIES II. $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID} = 2 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{array} \right.$								
Molality of acid potassium phthalate	$pK'_1$ (without overlapping corrections) <sup>a</sup>				$pK'_1$ (with overlapping corrections) <sup>b</sup>			
	Limiting law of Debye and Hückel	Guggenheim	3.76 A	3.76 A and $\beta$	Limiting law of Debye and Hückel	Guggenheim	3.76 A	3.76 A and $\beta$
0.00081865-----	2.9343	2.9377	2.9383	2.9388	2.9483	2.9486	2.9491	2.9493
.0014005-----	2.9371	2.9409	2.9417	2.9422	2.9474	2.9486	2.9493	2.9495
.0014548-----	2.9376	2.9412	2.9420	2.9425	2.9475	2.9487	2.9495	2.9497
.0023517-----	2.9390	2.9430	2.9438	2.9445	2.9482	2.9502	2.9500	2.9500
.0024641-----	2.9395	2.9436	2.9445	2.9451	2.9473	2.9494	2.9502	2.9507
.0031025-----	2.9381	2.9430	2.9437	2.9443	2.9455	2.9479	2.9489	2.9483
.0036743-----	2.9393	2.9440	2.9451	2.9457	2.9482	2.9489	2.9499	2.9513
.0050000-----	2.9394	2.9446	2.9457	2.9465	2.9459	2.9490	2.9501	2.9507
.0071782-----	2.9381	2.9449	2.9450	2.9459	2.9443	2.9480	2.9493	2.9499
.0090000-----	2.9375	2.9436	2.9449	2.9458	2.9435	2.9475	2.9487	2.9493

SERIES III. MOLALITY OF *o*-PHTHALIC ACID=MOLALITY OF ACID POTASSIUM PHTHALATE=0.018

Molality of potassium chloride								
.005-----	2.9384	2.9417	2.9424	2.9427	2.9459	2.9490	2.9497	2.9500
.008-----	2.9377	2.9425	2.9435	2.9438	2.9456	2.9490	2.9496	2.9498
.010-----	2.9376	2.9423	2.9434	2.9436	2.9452	2.9489	2.9495	2.9500
.014-----	2.9372	2.9413	2.9421	2.9425	2.9433	2.9480	2.9487	2.9494
.018-----	2.9351	2.9404	2.9414	2.9421	2.9429	2.9481	2.9490	2.9494

SERIES IV.  $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID} = 0.018 \\ \text{MOLALITY OF ACID POTASSIUM PHTHALATE} = 0.009 \end{array} \right.$ 

0.0030-----	2.9406	2.9448	2.9457	2.9461	2.9463	2.9484	2.9491	2.9494
.0050-----	2.9384	2.9432	2.9441	2.9447	2.9440	2.9468	2.9476	2.9481
.0070-----	2.9382	2.9439	2.9450	2.9458	2.9440	2.9474	2.9485	2.9490
.0090-----	2.9361	2.9434	2.9446	2.9455	2.9430	2.9470	2.9482	2.9488
.0493-----	2.9210	2.9409	2.9443	2.9485	2.9278	2.9456	2.9490	2.9497

SERIES V.  $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID} = 1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = 1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{array} \right.$ 

Molality of acid potassium phthalate								
0.0009423-----	2.9406	2.9330	2.9340	2.9345	2.9468	2.9476	2.9482	2.9481
.0016280-----	2.9314	2.9367	2.9377	2.9383	2.9473	2.9489	2.9497	2.9491
.0026071-----	2.9360	2.9412	2.9422	2.9430	2.9463	2.9488	2.9498	2.9498
.0030788-----	2.9374	2.9427	2.9437	2.9445	2.9466	2.9494	2.9505	2.9507
.0036444-----	2.9346	2.9399	2.9411	2.9419	2.9450	2.9481	2.9492	2.9491
.0038552-----	2.9342	2.9396	2.9408	2.9417	2.9442	2.9473	2.9485	2.9481
.0041264-----	2.9354	2.9337	2.9420	2.9429	2.9451	2.9486	2.9491	2.9496
.0044082-----	2.9362	2.9417	2.9429	2.9438	2.9439	2.9484	2.9495	2.9493
.0054960-----	2.9368	2.9421	2.9440	2.9450	2.9438	2.9476	2.9488	2.9488
.0059467-----	2.9367	2.9427	2.9439	2.9450	2.9439	2.9477	2.9489	2.9490

<sup>a</sup> The different values of  $pK'_1$  do not converge to a single value in the limit of infinite dilution or zero ionic strength.

<sup>b</sup> The different values of  $pK'_1$  do not converge to a single value in the limit of infinite dilution or zero ionic strength. The limiting values of  $pK_1$  at infinite dilution obtained by the "limiting-law" of Debye and Hückel and with the use of  $a_i=3.76$  A and  $\beta$  values differ by 0.0006; this difference being real. The value of  $pK_1$  obtained with the use of  $a_i$  and  $\beta$  is accepted as the better value.

The values of  $pK'_1$  calculated by the various methods are quite different. In figure 1 the "limiting-law" values (curve A) and the

"complete" values (curve *B*) are shown plotted as functions of the ionic strength for 25° C. In the range of low concentration the plots exhibit a marked curvature which arises from the neglect of "overlapping corrections." If this curvature is ignored, a straight line through the other points gives  $pK_1=2.9388$  by the limiting law and  $pK_1=2.9471$  by the complete treatment on extrapolation to infinite dilution or zero ionic strength. These values correspond, respectively, to values of 0.001151 and 0.001130 for  $K_1$ , which differ by

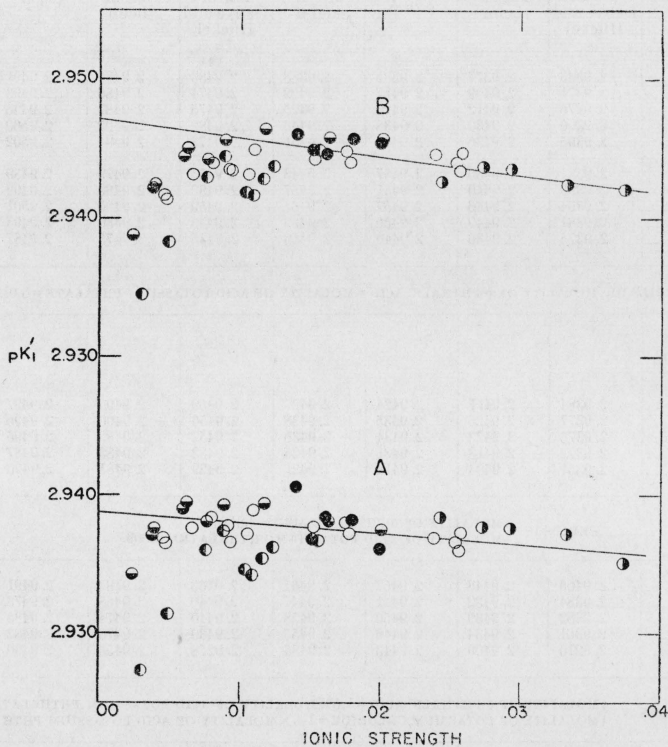


FIGURE 1.—Plots of the values of  $pK'_1$  as a function of the ionic strength of the solutions at 25° C without corrections for the amounts of phthalate ion in the solutions.

A, Values obtained by using the limiting law of Debye and Hückel for the ionic activity coefficients; B, values obtained by using the Hückel extension of the Debye-Hückel equation for the ionic activity coefficients in which  $a_i=3.76$  Å,  $\beta_H=-0.10$ ,  $\beta_{Cl}=-0.10$ ,  $\beta_{HPh}=-0.023$ , and  $\beta_{Ph}=-0.38$ .

○ = Series I.                      ● = Series IV.  
◐ = Series II.                    ◐ = Series V.  
◑ = Series III.

approximately 2 percent. In other words, the values of  $pK'_1$  calculated by the limiting law and by the complete treatment do not converge to the same value when they are plotted against the ionic strength.

These values of  $K_1$  and the same data for  $m_H$  previously used are then employed in eq 15 to calculate values of  $m_{Ph}$ , which are then inserted in eq 10 and 11 to obtain new values of  $m_{H_2Ph}$  and  $m_{HPh}$ . These in turn are used in eq 17 to calculate values of  $pK'_1$ . The "limiting-law" and "complete" values are shown plotted in part I of figure 2 as functions of the ionic strength at 25° C.



The curvatures of figure 1 have been eliminated by the corrections for  $m_{\text{Ph}}$ . Extrapolations to infinite dilution can then be made with certainty. The "limiting-law" values give  $pK_1=2.9469$  and the "complete" values give  $pK_1=2.9491$ , which correspond, respectively, to 0.001130 and 0.001124 for  $K_1$ , which differ by approximately 0.6 percent. Again, convergence has not been obtained. However, the assigned ionic strength and  $m_{\text{H}}$  of the solutions are altered by taking into account the presence of the diphtalate ion.

Repeating all the above processes with the new ionic strength gives new values of  $pK'_1$ , which are given in table 6 for a temperature of 25° C in the columns labeled "with overlapping" corrections. In figure 2,

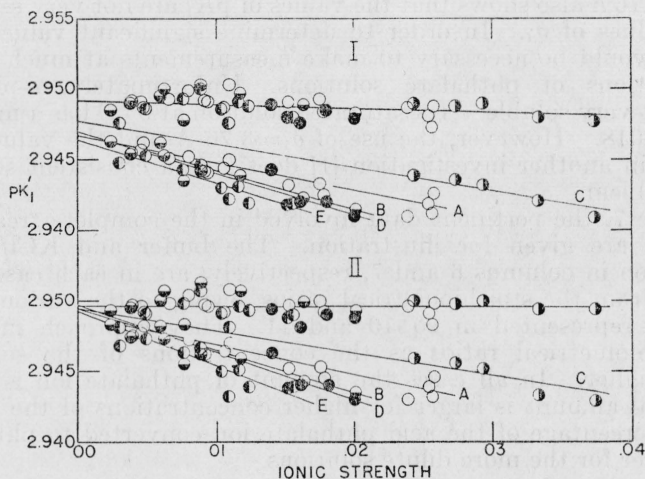


FIGURE 2.—Plots of the values of  $pK'_1$  for 25° C with corrections for the amounts of phthalate ion present in the solutions as a function of the ionic strength of the solutions.

Part I, Data based upon values of the hydrogen-ion concentration calculated without corrections for the amount of phthalate ion; part II, data based upon values of the hydrogen-ion concentration calculated with corrections for the amount of phthalate ion; upper curves, values obtained by using the Hückel extension of the Debye-Hückel equation for the ionic activity coefficients in which  $a_i=3.76$  Å,  $\beta_{\text{H}}=-0.10$ ,  $\beta_{\text{C}_1}=-0.10$ ,  $\beta_{\text{HPh}}=-0.023$ , and  $\beta_{\text{Ph}}=-0.38$ ; lower curves, values obtained by using the limiting law of Debye and Hückel for the ionic activity coefficients.

○ = Series I (A)                      ● = Series IV (D)  
 ◐ = Series II (B)                    ◐ = Series V (E)  
 ● = Series III (C)

part II, the final or complete values of  $pK'_1$ , are shown plotted with respect to the ionic strength. Extrapolation to zero ionic strength gives  $pK_1=2.9490$  (on the average) by the limiting law and  $pK_1=2.9496$  by the complete method. These values correspond, respectively, to 0.001125 and 0.001123 for  $K_1$ . Exact convergence of the  $pK'_1$  again has not been obtained. However, as  $a_i$  was shown to have a value of 3.76 Å in a previous paper [1], it is believed that values of  $pK$  obtained with its use are the correct values.<sup>6</sup>

<sup>6</sup> Lack of convergence of  $pK'$  values calculated by the limiting law or with the use of some  $a_i$  value is not restricted to the present case. The data obtained by Nims [27] for the first dissociation constant of phosphoric acid and by Hamer [3] for the bisulfate ion likewise show lack of convergence to a single thermodynamic value of the dissociation constant when the limiting law or some value of  $a_i$  is used. The lack of convergence is greater for the bisulfate ion than for phosphoric acid because its dissociation constant has a higher value. The lack of convergence arises from the fact that extrapolation must be made with data for different buffer ratios caused by the corrections for hydrogen-ion concentration. As values of  $a_i$  are not known for the first dissociation of phosphoric acid and sulfuric acid there is some uncertainty about the values of the dissociation constants of these acids. This uncertainty about the value of  $a_i$  to use is believed to be eliminated in the present case.

The values of  $pK'_1$  calculated by the limiting law are dependent upon the ionic strength whereas those calculated by the complete method are not. The complete treatment is quite insensitive to the values of  $\beta$ , however, and hence gives only a qualitative confirmation of the accuracy of the  $\beta$  values determined in the investigation of the second dissociation constant of *o*-phthalic acid. Comparison of the values of  $pK_1$  given in the last 2 columns of table 6 show that the values of  $pK_1$  calculated with or without the use of the  $\beta$  values are not appreciably different.

Comparison of the data of column 7 obtained with an  $a_i$  value of 3.00 A (Guggenheim values) and of column 8 obtained with an  $a_i$  value of 3.76 A also shows that the values of  $pK_1$  are not very sensitive to the values of  $a_i$ . In order to determine significant values of  $a_i$  and  $\beta$  it would be necessary to make measurements at much higher concentrations of phthalate solutions. Unfortunately, *o*-phthalic acid is not very soluble. Its saturated solution at 0° C has a molality of only 0.018. However, the use of  $a_i=3.76$  A and the values of  $\beta$  obtained in another investigation [1] does give a consistent solution of the problem.

In table 7, the pertinent data involved in the complete treatment at 25° C are given for illustration. The buffer and KCl/KHPh ratios given in columns 6 and 7, respectively, are in each case quite different from the stoichiometrical ratios, owing to the various ionic equilibria represented in eq 10 and 11. They approach in value the stoichiometrical ratios as the concentrations of the solutions become higher. In all cases the amount of phthalate ion is small. The actual amount is larger for higher concentrations of the buffer, but the percentage of the acid phthalate ion converted to phthalate ion is larger for the more dilute solutions.

TABLE 7.—Summary of the values of the concentrations of the ionic and molecular species of phthalate-chloride mixtures and of the first dissociation constant of *o*-phthalic acid at 25° C

SERIES I.  $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID} = 1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{array} \right.$

Molality of acid potassium phthalate	Molality of undissociated <i>o</i> -phthalic acid	Molality of acid phthalate ion	Molality of phthalate ion	Molality of hydrogen ion	H <sub>2</sub> Ph HPh	KCl HPh	$K'_1 \times 10^3$ (without corrections for activity coefficients)	$K'_1 \times 10^3$ (with Debye-Hückel limiting law corrections)	$K'_1 \times 10^3$ (with corrections for activity coefficients when $a_{\pm}=3.76$ A)	$K'_1 \times 10^3$ (with total corrections for activity coefficients)
0.0018357	0.0018696	0.0027032	0.000015	0.00089854	0.6911	0.6786	1.3001	1.1090	1.1228	1.1231
0.0019071	0.0019604	0.0027918	0.000016	0.00091588	.7022	.6831	1.3043	1.1095	1.1237	1.1241
0.0027658	0.0030859	0.0038103	0.000017	0.0010810	.8099	.7259	1.3348	1.1027	1.1219	1.1225
0.0034165	0.0039653	0.0045572	0.000019	0.0011782	.8701	.7497	1.3540	1.0970	1.1200	1.1210
0.0039521	0.0047005	0.0051569	0.000023	0.0012506	.9115	.7664	1.3720	1.0956	1.1222	1.1228
0.0040518	0.0048653	0.0052539	0.000026	0.0012738	.9260	.7712	1.3755	1.0952	1.1223	1.1231
0.0046056	0.0056086	0.0058772	0.000028	0.0013279	.9543	.7836	1.3915	1.0931	1.1234	1.1241
0.0047953	0.0058731	0.0060946	0.000031	0.0013406	.9637	.7868	1.3912	1.0881	1.1194	1.1200
0.0068606	0.0087979	0.0083211	0.000032	0.0013255	1.0373	.8245	1.4428	1.0793	1.1219	1.1228
0.0079547	0.010369	0.0094885	0.000033	0.0016001	1.0927	.8383	1.4643	1.0779	1.1211	1.1220
0.0081020	0.010574	0.0096357	0.000040	0.0016131	1.0974	.8408	1.4699	1.0780	1.1231	1.1241
0.011058	0.014924	0.012741	0.000050	0.0017820	1.1713	.8679	1.5217	1.0582	1.1218	1.1231
0.011799	0.016007	0.013512	0.000053	0.0018189	1.1847	.8732	1.5354	1.0557	1.1229	1.1243
0.011913	0.016175	0.013622	0.000060	0.0018290	1.1874	.8745	1.5403	1.0570	1.1252	1.1264
0.012000	0.016229	0.013724	0.000047	0.0018165	1.1825	.8744	1.5361	1.0528	1.1211	1.1225

SERIES II.  $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID} = 2 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{array} \right.$

0.00081865	0.00090865	0.0015352	0.000012	0.00074083	0.5919	0.5333	1.2517	1.1159	1.1232	1.1238
0.0014005	0.0018234	0.0023656	0.000012	0.00099005	.7708	.5920	1.2845	1.1119	1.1229	1.1233
0.0014548	0.0019128	0.0024392	0.000012	0.0010090	.7842	.5964	1.2867	1.1107	1.1225	1.1228
0.0023517	0.0034476	0.0035933	0.000014	0.0012700	.9595	.6545	1.3237	1.1039	1.1216	1.1220
0.0024641	0.0036463	0.0037332	0.000015	0.0012947	.9767	.6601	1.3256	1.1014	1.1196	1.1202
0.0031025	0.0047844	0.0045043	0.000017	0.0014393	1.0622	.6888	1.3550	1.1034	1.1258	1.1264
0.0036743	0.0058295	0.0051775	0.000018	0.0015350	1.1259	.7097	1.3633	1.0923	1.1181	1.1187
0.0050000	0.0082841	0.0066995	0.000019	0.0017324	1.2365	.7463	1.4010	1.0862	1.1195	1.1202
0.0071782	0.012403	0.0091054	0.000026	0.0019795	1.3622	.7883	1.4532	1.0763	1.1215	1.1223
0.0090000	0.015896	0.011068	0.000036	0.0021404	1.4362	.8132	1.4904	1.0677	1.1224	1.1238

See footnote at end of table.

TABLE 7.—Summary of the values of the concentrations of the ionic and molecular species of phthalate-chloride mixtures and of the first dissociation constant of *o*-phthalic acid at 25° C—ContinuedSERIES III. MOLALITY OF *o*-PHTHALIC ACID=MOLALITY OF ACID POTASSIUM PHTHALATE=0.018.

Molality of potassium chloride	Molality of undissociated <i>o</i> -phthalic acid	Molality of acid phthalate ion	Molality of phthalate ion	Molality of hydrogen ion	H <sub>2</sub> Ph HPH	KCl HPH	$K'_1 \times 10^3$ (without corrections for activity coefficients)	$K'_1 \times 10^3$ (with Debye-Hückel limiting law corrections)	$K'_1 \times 10^3$ (with corrections for activity coefficients when $a_{\pm}=3.76$ A)	$K'_1 \times 10^3$ (with total corrections for activity coefficients)
0.005-----	0.016765	0.019135	0.000100	0.0013352	0.8761	0.2613	1.5239	1.0559	1.1205	1.1221
.008-----	.016733	.019185	.000082	.0013497	.8722	.4170	1.5478	1.0492	1.1212	1.1225
.010-----	.016734	.019169	.000097	.0013639	.8730	.5217	1.5623	1.0441	1.1205	1.1221
.014-----	.016694	.019236	.000071	.0013819	.8678	.7278	1.5924	1.0332	1.1199	1.1236
.018-----	.016689	.019214	.000096	.0014062	.8686	.9368	1.6190	1.0276	1.1221	1.1238

SERIES IV.  $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID}=0.018. \\ \text{MOLALITY OF ACID POTASSIUM PHTHALATE}=0.009. \end{array} \right.$ 

0.0030-----	0.015960	0.011005	0.000035	0.0020756	1.4502	0.2726	1.4312	1.0830	1.1225	1.1236
.0050-----	.015938	.011013	.000049	.0021096	1.4472	.4540	1.4577	1.0816	1.1265	1.1269
.0070-----	.015912	.011052	.000036	.0021206	1.4397	.6334	1.4729	1.0735	1.1233	1.1246
.0090-----	.015895	.011067	.000037	.0021431	1.4363	.8132	1.4921	1.0689	1.1237	1.1251
.0493-----	.015601	.011412	.000005	.0023879	1.3671	4.3200	1.7467	0.9789	1.1210	1.1228

SERIES V.  $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID}=1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE}=1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{array} \right.$ 

Molality of acid potassium phthalate										
0.0009423-----	0.00078617	0.0015553	0.000014	0.00064143	0.5055	0.9088	1.2690	1.1156	1.1249	1.1251
.0016280-----	.0016036	.0024479	.000015	.00085693	.6551	.9976	1.3081	1.1091	1.1238	1.1243
.0026071-----	.0028631	.0036406	.000016	.0010614	.7864	1.0742	1.3497	1.1001	1.1221	1.1225
.0030788-----	.0034930	.0041919	.000018	.0011372	.8333	1.1017	1.3647	1.0944	1.1197	1.1202
.0036444-----	.0042636	.0048186	.000020	.0012306	.8848	1.1345	1.3908	1.0950	1.1248	1.1243
.0038552-----	.0045589	.0050506	.000024	.0012521	.9026	1.1450	1.3872	1.0855	1.1164	1.1170
.0041264-----	.0049275	.0053610	.000025	.0012897	.9191	1.1546	1.4032	1.0894	1.1222	1.1231
.0044082-----	.0053180	.0056764	.000025	.0013224	.9369	1.1649	1.4115	1.0871	1.1221	1.1238
.0054960-----	.0068326	.0068883	.000025	.0014336	.9919	1.1968	1.4453	1.0821	1.1241	1.1251
.0056467-----	.0070466	.0070449	.000026	.0014487	1.0002	1.2023	1.4484	1.0805	1.1237	1.1246

\* Molality of *o*-phthalic acid = 1.5063 × molality of acid potassium phthalate and molality of potassium chloride = molality of acid potassium phthalate.



From the results of series III and IV, it was found that additions of potassium chloride to a solution of the same buffer ratio lowers the pH value of the solutions, causes a decrease in the amounts of undissociated *o*-phthalic acid and phthalate ion, and produces increases in the amounts of acid phthalate and hydrogen ions. In other words the tendency of reaction 7 to proceed from left to right is decreased by the addition of potassium chloride. In figure 3, the values of  $pK'_1$  with and without corrections for activity coefficients are shown plotted as functions of the ionic strength for 25° C. All the data

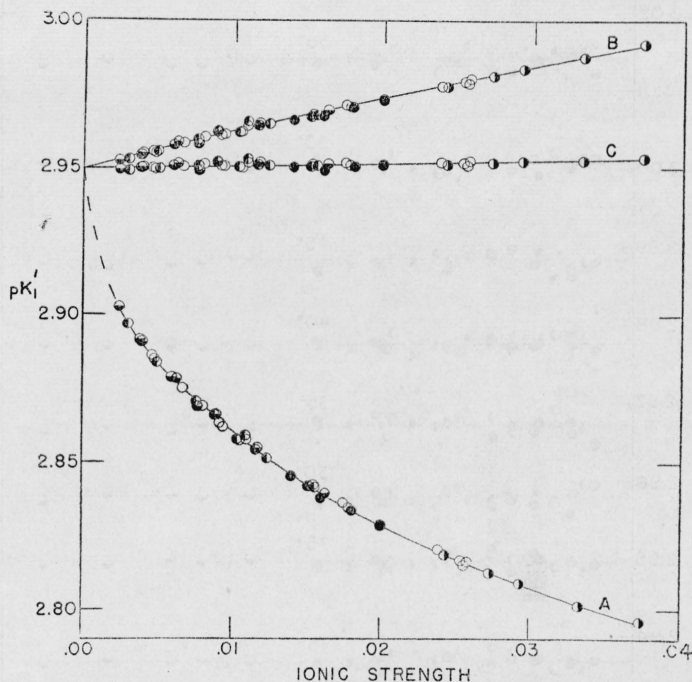


FIGURE 3.—Plots of the values of  $pK'_1$  for 25° C as a function of the ionic strength of the solution.

In each case, the same values of the ionic and molecular species were employed.

A, Without corrections for activity coefficients; B, with corrections for activity coefficients based upon the limiting law of Debye and Hückel; C, with corrections for the activity coefficients based upon the Debye-Hückel equation in which  $a_i = 3.76$  Å.

The values for the various series of experiments fall on the same curves for the scale used in the construction of the graph.

extrapolate to the same limiting value for  $pK_1$ . These curves are based upon the same values of the ionic and molecular species (calculated by the complete method) whereas the data plotted in figures 1 and 2 were for different values of the ionic and molecular species. For this reason convergence of the values of  $pK'_1$  to a single thermodynamic value at infinite dilution is obtained.

In figure 4 the values obtained by the complete method are shown plotted as functions of the ionic strength at several other temperatures. The average values of  $pK_1$  with the mean deviation for series I, II, and V are given in table 8. The average of the three determinations and the total mean deviation is given in column 5 for each tem-

perature. The deviations range from 0.0005 to 0.0011, which correspond to 0.03–0.07 mv in the emf. Values of the first dissociation constant of *o*-phthalic acid are given in the last column of the table.

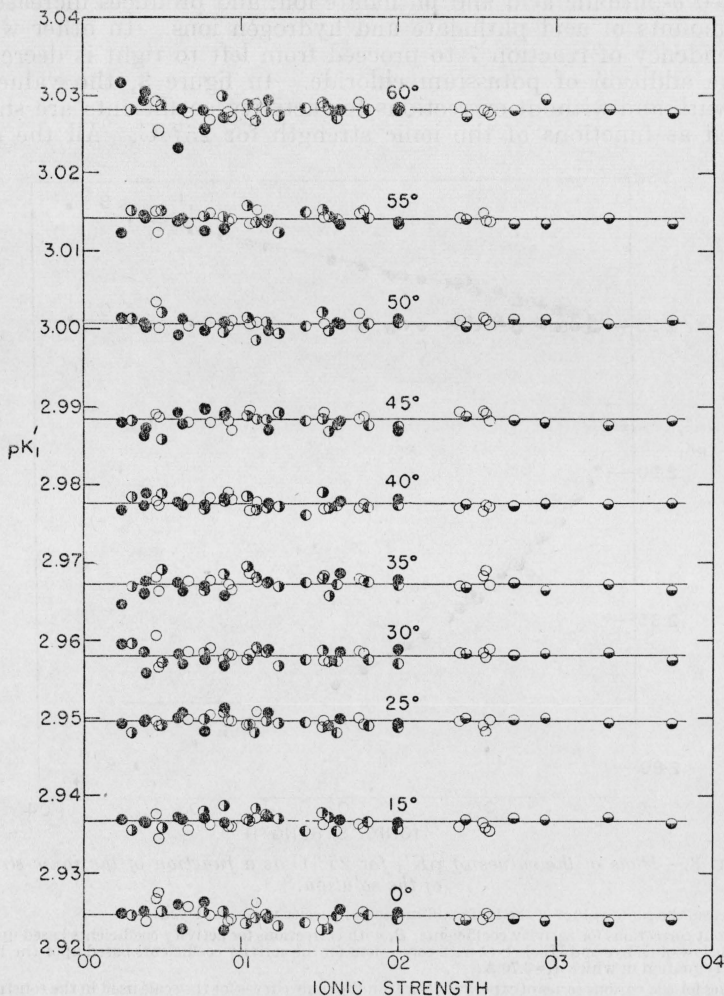


FIGURE 4.—Plots of the values of  $pK'_1$  calculated by the complete method for several temperatures as a function of the ionic strength of the solutions.

○ = Series I.                      ● = Series IV.  
 ◐ = Series II.                    ◑ = Series V.  
 ⊙ = Series III.

In table 9 the values of  $K_1$  are compared with those obtained by other investigators at 18° and 25° C. A critical comparison is not possible as previous investigations were restricted to a single temperature and involved a number of uncertainties.

TABLE 8.—Summary of numerical values of  $pK_1$  and  $K_1$  calculated from measurements of three different buffer ratios at temperatures of 0° to 60° C

Temperature	$pK_1$				$K_1 \times 10^3$
$t^\circ \text{C}$	Series I	Series II	Series V	Average	
0.....	2.9250 $\pm 0.0009$	2.9246 $\pm 0.0014$	2.9241 $\pm 0.0007$	2.9246 $\pm 0.0010$	1.190
5.....	2.9273 $\pm 0.0006$	2.9269 $\pm 0.0008$	2.9276 $\pm 0.0010$	2.9273 $\pm 0.0008$	1.182
10.....	2.9316 $\pm 0.0005$	2.9308 $\pm 0.0008$	2.9319 $\pm 0.0009$	2.9314 $\pm 0.0008$	1.171
15.....	2.9361 $\pm 0.0005$	2.9368 $\pm 0.0006$	2.9373 $\pm 0.0007$	2.9367 $\pm 0.0006$	1.157
20.....	2.9430 $\pm 0.0004$	2.9426 $\pm 0.0008$	2.9432 $\pm 0.0006$	2.9429 $\pm 0.0006$	1.141
25.....	2.9496 $\pm 0.0004$	2.9499 $\pm 0.0005$	2.9492 $\pm 0.0006$	2.9496 $\pm 0.0005$	1.123
30.....	2.9584 $\pm 0.0005$	2.9577 $\pm 0.0009$	2.9580 $\pm 0.0008$	2.9580 $\pm 0.0008$	1.102
35.....	2.9677 $\pm 0.0005$	2.9663 $\pm 0.0014$	2.9677 $\pm 0.0010$	2.9672 $\pm 0.0010$	1.078
40.....	2.9775 $\pm 0.0006$	2.9773 $\pm 0.0005$	2.9781 $\pm 0.0008$	2.9776 $\pm 0.0007$	1.053
45.....	2.9887 $\pm 0.0006$	2.9879 $\pm 0.0008$	2.9884 $\pm 0.0008$	2.9884 $\pm 0.0008$	1.027
50.....	3.0010 $\pm 0.0006$	3.0005 $\pm 0.0007$	3.0005 $\pm 0.0011$	3.0007 $\pm 0.0008$	0.998
55.....	3.0143 $\pm 0.0006$	3.0136 $\pm 0.0006$	3.0146 $\pm 0.0006$	3.0142 $\pm 0.0006$	.968
60.....	3.0279 $\pm 0.0007$	3.0282 $\pm 0.0017$	3.0284 $\pm 0.0007$	3.0282 $\pm 0.0011$	.937

\* Arithmetical mean deviation.

TABLE 9.—Numerical values of the first dissociation constant of *o*-phthalic acid obtained by different workers at 18° and 25° C

Year	Observer and reference	Method	$K_1 \times 10^3$	
			18°C	25°C
1889	W. Ostwald, Z. physik. Chem. <b>3</b> , 369 (1889).....	Conductivity.....	1.21	-----
1891	D. Berthelot, Ann. chim. phys. [6] <b>23</b> , 5 (1891).....	do.....	1.25	-----
1892	J. E. Trevor, Z. physik. Chem. <b>10</b> , 321 (1892).....	Sucrose inversion.....	-----	1.21
1908	E. E. Chandler, J. Am. Chem. Soc. <b>30</b> , 694 (1908).....	Conductivity.....	-----	1.21
1908	E. Salm, Z. physik. Chem. <b>63</b> , 83 (1908).....	Indicators.....	-----	1.3
* 1909	G. F. White and H. C. Jones, Am. Chem. J. <b>42</b> , 520 (1909).....	Conductivity.....	-----	1.26
1910	A. C. D. Rivett and N. V. Sidgwick, J. Chem. Soc. <b>97</b> , 1677 (1910).....	Velocity of hydration of the anhydride.....	-----	1.21
1924	E. Larsson, Z. anorg. allgem. Chem. <b>140</b> , 292 (1924).....	Potentiometric titration.....	1.20	-----
1925	M. Mizutani, Z. physik. chem. <b>118</b> , 318 (1925).....	do.....	b 1.7	-----
1928	R. Kuhn and A. Wasserman, Helv. chim. Acta <b>11</b> , 44 (1928).....	emf-quinhydrone electrode.....	-----	1.3
1929	A. Ölander, Z. physik. Chem. Abt. [A] <b>144</b> , 49 (1929).....	Potentiometric titration.....	-----	* 1.0
1935	W. R. Maxwell and J. R. Partington, Trans. Faraday Soc. <b>31</b> , 922 (1935).....	do.....	-----	1.05
1945	Present investigation.....	Galvanic cells without liquid junction.....	d 1.149	1.123

\* These authors obtained 0.00134 and 0.00122 for  $K_1$  at 0° and 35° C, respectively.

b Value for 20° C.

c Value for 50° C.

d Value calculated by eq 19.

In figure 5, the values of  $pK_1$  are shown plotted as a function of the temperature in degrees centigrade. This variation may be expressed by the Harned-Robinson [17] equation

$$pK_1 = A^*/T + B + CT. \quad (18)$$

The constants of this equation were obtained by the method of least squares by using the average values of  $pK_1$  given in column 5 of table 8. The values of  $pK_1$  are given with a mean deviation of 0.0003 by the equation

$$pK_1 = 561.57/T - 1.2843 + 0.0078833T, \quad (19)$$

where  $T = t^\circ \text{C} + 273.16$ .

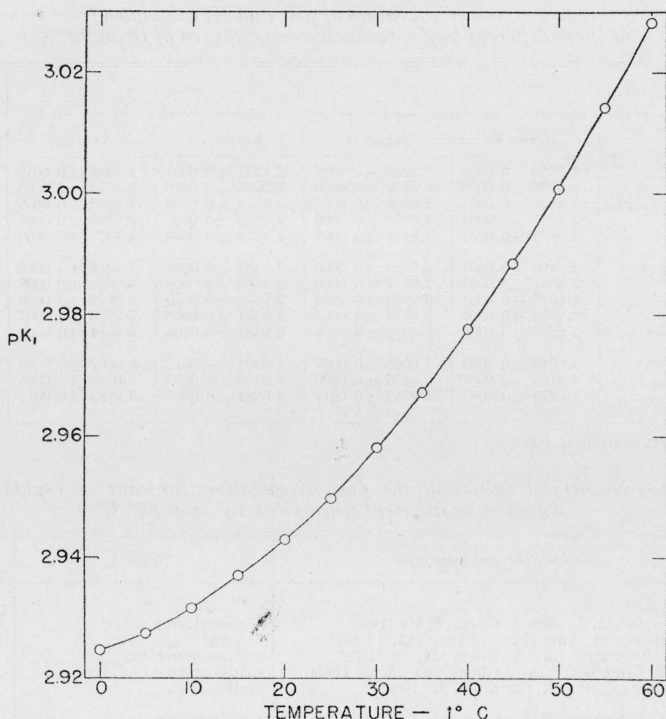


FIGURE 5.—Plot of the average values of  $pK_1$  with respect to temperature in degrees centigrade.

#### V. THERMODYNAMIC QUANTITIES FOR THE PROCESS: o-PHTHALIC ACID $\rightleftharpoons$ HYDROGEN ION + ACID PHTHALATE ION

Thermodynamic quantities for the process  $H_2Ph \rightleftharpoons H^+ + HPh^-$  can be computed from the equations of Harned and Robinson. The change in free energy,  $\Delta F^\circ$ ; in heat content,  $\Delta H^\circ$ ; in entropy,  $\Delta S^\circ$ ; and in heat capacity,  $\Delta C_p^\circ$ ; for the dissociation of 1 mole of  $H_2Ph$  for the standard state are given, respectively, in international joules by the equations

$$\Delta F^\circ = -RT \ln K_1 = 2.3026R(A^* + BT + CT^2),$$

$$= 10\,748.9 - 24.5826T + 0.15089T^2 \quad (20)$$

$$\Delta S^\circ = - (d\Delta F^\circ/dT) = 2.3026R(-B - 2CT),$$

$$= 24.58 - 0.30178T, \quad (21)$$

$$\Delta H^\circ = \Delta F^\circ + T\Delta S^\circ = 2.3026R(A^* - CT^2),$$

$$= 10\,748.9 - 0.15089T^2, \quad (22)$$

$$\Delta C_p^\circ = (d\Delta H^\circ/dT) = 2.3026R(-2CT),$$

$$= -0.3018T, \quad (23)$$

where  $A^*$ ,  $B$ , and  $C$  are the same constants as in eq 18.

These quantities were calculated in terms of the international joule by using a value of  $8.3127 \text{ int. j deg}^{-1}$  for  $R$  [18] and are given in table 10. They were also calculated in terms of a defined calorie, 1 cal being taken equal to  $4.1833 \text{ int. j}$ , in accordance with the recommendation of the International Union of Chemistry [19,20].



These are also listed in table 10. The values of  $\Delta C_p^\circ$  increase slightly with temperature, as predicted by a semiempirical equation derived by Moelwyn-Hughes [21]. Values of  $\Delta F^\circ$  and  $\Delta S^\circ$  also increase with respect to temperature.

TABLE 10.—*Thermodynamic data from 0° to 60° C for the dissociation of o-phthalic acid into hydrogen and acid phthalate ions*

t°C	$\Delta F^\circ$		$\Delta H^\circ$		$\Delta S^\circ$		$\Delta C_p^\circ$	
	Int. j	cal	Int. j	cal	Int. j	cal	Int. j	cal
0.....	15,293	3,656	-510	-122	-57.9	-13.8	-82.4	-19.7
5.....	15,586	3,726	-926	-221	-59.4	-14.2	-84.0	-20.1
10.....	15,886	3,798	-1,349	-323	-60.9	-14.6	-85.5	-20.4
15.....	16,195	3,871	-1,780	-426	-61.4	-14.7	-87.0	-20.8
20.....	16,510	3,947	-2,219	-530	-63.9	-15.3	-88.5	-21.2
25.....	16,833	4,024	-2,665	-637	-65.4	-15.6	-90.0	-21.5
30.....	17,164	4,103	-3,119	-746	-66.9	-16.0	-91.5	-21.9
35.....	17,502	4,184	-3,580	-856	-68.4	-16.4	-93.0	-22.2
40.....	17,848	4,267	-4,049	-968	-69.9	-16.7	-94.5	-22.6
45.....	18,202	4,351	-4,525	-1,082	-72.4	-17.3	-96.0	-23.0
50.....	18,563	4,437	-5,009	-1,197	-72.9	-17.4	-97.5	-23.3
55.....	18,931	4,525	-5,500	-1,315	-74.5	-17.8	-99.0	-23.7
60.....	19,307	4,615	-5,999	-1,434	-76.0	-18.2	-100.6	-24.0

The values of  $\Delta F^\circ$  are obtained directly from those for  $K_1$ . The uncertainties in  $K_1$  introduce deviations in the values of  $\Delta F^\circ$  of only 0.1 percent, or about 17 int. j or 4 calories. The values of  $\Delta H^\circ$  and  $\Delta C_p^\circ$  are subject to large error, estimated to be of the order of 100 calories in  $\Delta H^\circ$  and 3 calories in  $\Delta C_p^\circ$ . The error in  $\Delta S^\circ$  is determined by the uncertainties in  $\Delta H^\circ$  and  $\Delta C_p^\circ$  and is approximately 0.3 calorie.

Unfortunately, no calorimetric measurements have been made of the heat of dissociation of *o*-phthalic acid or of the heat capacities of the ions and molecule involved in the dissociation with which comparisons may be made. However, certain comparisons may be made with similar data obtained for the first dissociation of other acids. Pitzer [22] found from theoretical considerations that  $\Delta C_p^\circ$  and  $\Delta S^\circ$  are respectively -40 cal/deg and -22 cal for the dissociation of molecules into ions. Experimental measurements [23] for a great number of monobasic acids agree very well with these values. However for the first dissociation of *o*-phthalic acid  $\Delta C_p^\circ$  is -21.5 cal/deg which is about one-half the theoretical value given by Pitzer. However inductive and tautomeric effects in phthalic acid (substituted benzoic acid) will tend to increase the electrostatic potential at the carboxyl group [24] producing an orientation of the solvent ( $H_2O$ ) molecules near the surface of the carboxyl groups. Also the steric factors will tend to reduce the value of  $\Delta C_p^\circ$ , the tendency being most marked for substitution in the orthoposition because of a greater effect on the orientation of the solvent molecules near the carboxyl groups [24].

Everett and Wynne-Jones [24] determined the value of  $\Delta C_p^\circ$  for a number of substituted benzoic acids. They found that the meta- and para-substituted acids had values of  $\Delta C_p^\circ$  of about -37 cal/deg, whereas, the orthosubstituted acids had values of  $\Delta C_p^\circ$  of about -25 cal/deg, on the average. As *o*-phthalic acid may be considered to be carboxylic-substituted benzoic acid, its value of  $\Delta C_p^\circ$  of -21.5 cal/deg is in line with the values for other orthosubstituted benzoic acids.

In table 11, a comparison of  $\Delta C_p^\circ$  and  $\Delta S^\circ$  for a number of ortho-substituted benzoic acids is given. With the exception of salicylic acid, the data of the different acids are almost the same. Everett and Wynne-Jones state that the  $\text{OH}^-$  group favors the orientation of the water molecule, probably because the hydroxyl group forms a hydrogen bond with the oxygen of a water molecule. Therefore, the  $\Delta C_p^\circ$  value will be higher for salicylic acid than for those acids not capable of producing hydrogen bonding. The value of  $\Delta S^\circ$  for *o*-phthalic acid is somewhat less than that for the other substituted acids. The reason for this is not quite clear. However, within the experimental error with which  $\Delta S^\circ$  is determined in the two sets of measurements, the values may be considered to be within substantial agreement.

TABLE 11.—Comparison of values of  $\Delta C_p^\circ$ ,  $\Delta S^\circ$ ,  $\Delta F^\circ$ , and  $\text{pK}$  at  $25^\circ\text{C}$  for ortho-substituted benzoic acids <sup>a</sup>

Substituent	Acid	$\Delta C_p^\circ$	$\Delta S^\circ$	$\Delta F^\circ$	$\text{pK}$
		<i>cal/deg</i>	<i>cal/deg</i>	<i>cal</i>	
Cl.....	Benzoic.....	-36.2	-18.9	5,682	4.17
I.....	Chlorobenzoic.....	-28.3	-21.5	3,926	2.88
NO <sub>2</sub> .....	Iodobenzoic.....	-21.9	-24.0	3,903	2.86
OH.....	Nitrobenzoic.....	-23.7	-21.3	2,980	2.18
COOH.....	Salicylic.....	-47.7	-10.2	4,055	2.97
	Phthalic.....	-21.5	-15.6	4,024	2.95

<sup>a</sup> All the values are taken from a paper by Everett and Wynne-Jones [24], except those for phthalic acid, which are from the present investigation.

## VI. INTERCARBOXYLIC DISTANCES IN *o*-PHTHALIC ACID

The linear distance  $r$  between the ionic centers of the carboxyl groups of a rigid dibasic acid may be computed by the Bjerrum equation [25] <sup>7</sup>

$$\log (K_1/K_2) - \log 4 = \epsilon^2 / (2.3026 D r k T), \quad [24]$$

where  $K_1$  and  $K_2$  are the first and second dissociation constants of the dibasic acid,  $D$  is the dielectric constant of the solvent,  $k$  is the Boltzmann constant ( $1.380 \times 10^{-16}$  erg deg<sup>-1</sup>),  $T$  is the absolute temperature, and  $\epsilon$  is the electronic charge ( $4.8025 \times 10^{-10}$  abs esu).

Values of  $r$  for *o*-phthalic acid were computed by this equation for each temperature by the use of the values of  $K_1$  obtained in this investigation and the values of  $K_2$  given in another publication [1]. They are given in table 12. Within the experimental error the values are independent of the temperature. The average value of 1.66 Å is, as anticipated, somewhat larger than 1.53 Å and 1.43 Å as found by X-ray measurements for the distances, respectively, between the carbon atoms in the diamond and in benzene, but is of the expected order of magnitude.

<sup>7</sup> More complicated equations may be employed to relate chemical constitution with dissociation constants. See Gustav Kortüm, *Elektrolytlösungen*, chap. 15, for a review of these equations. (Akademische Verlagsgesellschaft, Becker & Erler, Kom.-Ges., Leipzig, 1941).

TABLE 12.—Numerical values of the intercarboxyl distances in *o*-phthalic acid at temperatures of 0° to 60° C \*

<i>t</i> °C	$K_1 \times 10^3$	$K_2 \times 10^6$	$K_1/K_2$	$r_i$ Bjerrum Angstroms
0.....	1.190	3.696	322	1.58
5.....	1.182	3.820	309	1.60
10.....	1.171	3.894	301	1.62
15.....	1.157	3.934	294	1.64
20.....	1.141	3.937	290	1.66
25.....	1.123	3.906	288	1.67
30.....	1.102	3.840	287	1.68
35.....	1.078	3.740	288	1.69
40.....	1.053	3.611	292	1.70
45.....	1.027	3.454	297	1.70
50.....	0.998	3.274	305	1.70
55.....	.968	3.075	315	1.70
60.....	.937	2.875	326	1.70

\* Distance between C atoms in the diamond=1.53. Distance between C atoms in benzene=1.43.

## VII. pH VALUES OF PHTHALATE-CHLORIDE SOLUTIONS

The pH value of each solution used in the cells was calculated from eq 12 by using

$$-2A\sqrt{\mu}/(1+3.76B\sqrt{\mu}) + \beta_C m_{Cl} + \beta_H m_H$$

for  $\log f_H f_{Cl}$ . The pH values for solutions of the various series of experiments are given in tables 13, 14, 15, 16, and 17. The values

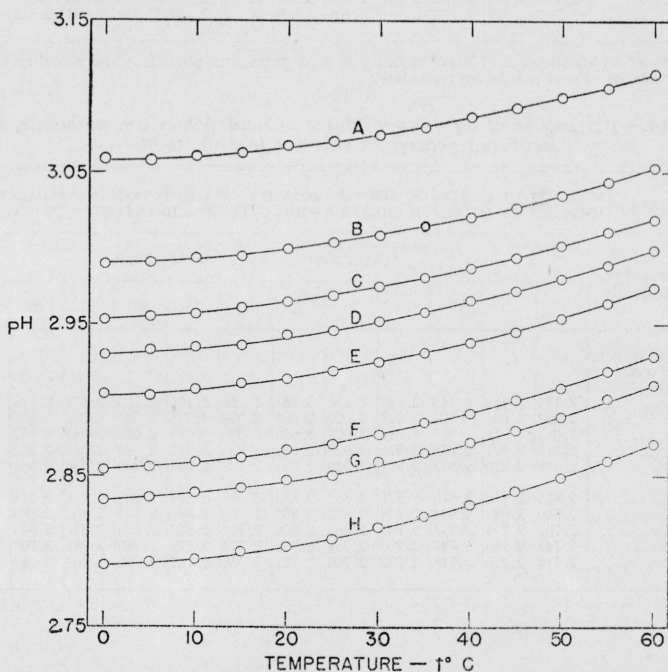


FIGURE 6.—Plot of a few of the pH values of solutions of series I with respect to temperature in degrees centigrade.

A=0.0019071-*m* KHPH.B=0.0027658-*m* KHPH.C=0.0034165-*m* KHPH.D=0.0039521-*m* KHPH.E=0.0047953-*m* KHPH.F=0.0068606-*m* KHPH.G=0.0081020-*m* KHPH.H=0.011799-*m* KHPH.E=0.0047953-*m* KHPH.F=0.0068606-*m* KHPH.G=0.0081020-*m* KHPH.H=0.011799-*m* KHPH.Molality of  $H_2Ph=1.5 \times$  molality of KHPH and molality of  $KCl$ =molality of KHPH.

range from 2.699 to 3.258 and have a low-temperature coefficient. On the average, the pH values differ by 0.07 pH unit between 0° and 60° C.

TABLE 13.—pH values of aqueous mixtures of acid potassium phthalate, *o*-phthalic acid and potassium chloride from 0° to 60° C

SERIES I. $\left\{ \begin{array}{l} \text{MOLALITY OF o-PHTHALIC ACID} = 1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \\ \text{MOLALITY OF POTASSIUM CHLORIDE} = \text{MOLALITY OF ACID POTASSIUM PHTHALATE.} \end{array} \right.$													
Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
	<i>Moles of solute per 1,000 g of water</i>												
0.0018357-----	3.066	3.066	3.068	3.072	3.075	3.078	3.084	3.089	3.094	3.101	3.109	3.116	3.124
.0019071-----	3.059	3.058	3.061	3.063	3.068	3.071	3.075	3.080	3.087	3.093	3.100	3.106	3.115
.0027658-----	2.990	2.991	2.994	2.995	3.000	3.004	3.009	3.015	3.021	3.027	3.035	3.044	3.053
.0034165-----	2.953	2.955	2.957	2.961	2.965	2.969	2.975	2.981	2.987	2.994	3.002	3.011	3.019
.0039521-----	2.930	2.933	2.935	2.936	2.943	2.946	2.952	2.958	2.966	2.972	2.980	2.989	2.999
•.0040518-----	2.924	2.926	2.928	2.931	2.936	2.939	2.945	2.951	2.958	2.964	2.974	2.983	2.991
.0046056-----	2.909	2.912	2.915	2.917	2.920	2.924	2.930	2.938	2.943	2.952	2.961	2.970	2.979
.0047953-----	2.904	2.903	2.907	2.911	2.914	2.919	2.925	2.931	2.938	2.945	2.954	2.964	2.974
.0068606-----	2.854	2.857	2.859	2.862	2.867	2.871	2.877	2.885	2.891	2.900	2.908	2.919	2.929
.0079547-----	2.838	2.838	2.843	2.845	2.850	2.854	2.861	2.865	2.864	2.883	2.894	2.903	2.914
.0081020-----	2.835	2.837	2.840	2.843	2.848	2.851	2.860	2.866	2.873	2.881	2.890	2.902	2.911
•.011058-----	2.796	2.800	2.802	2.806	2.811	2.816	2.823	2.830	2.837	2.846	2.856	2.866	2.878
•.011799-----	2.791	2.794	2.796	2.800	2.804	2.808	2.816	2.824	2.830	2.840	2.850	2.860	2.871
•.011913-----	2.790	2.793	2.795	2.799	2.804	2.807	2.815	2.826	2.831	2.839	2.849	2.859	2.871
.012000-----	2.792	2.794	2.796	2.801	2.804	2.809	2.817	2.824	2.832	2.841	2.849	2.861	2.872

• Molality of *o*-phthalic acid = 1.5063 × molality of acid potassium phthalate and molality of potassium chloride = molality of acid potassium phthalate.

TABLE 14.—pH values of aqueous mixtures of acid potassium phthalate, *o*-phthalic acid and potassium chloride from 0° to 60° C

SERIES II. { MOLALITY OF o-PHTHALIC ACID=2×MOLALITY OF ACID POTASSIUM PHTHALATE. MOLALITY OF POTASSIUM CHLORIDE=MOLALITY OF ACID POTASSIUM PHTHALATE.													
Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
<i>Moles of solute per 1,000 g of water</i>													
0.0008187-----	3.144	3.144	3.145	3.148	3.150	3.154	3.158	3.160	3.166	3.171	3.178	3.182	3.192
.0014005-----	3.022	3.024	3.024	3.027	3.029	3.033	3.038	3.038	3.048	3.053	3.061	3.068	3.076
.0014548-----	3.013	3.014	3.016	3.019	3.022	3.026	3.030	3.034	3.036	3.045	3.052	3.060	3.069
.0023517-----	2.919	2.921	2.923	2.925	2.928	2.932	2.936	2.942	2.948	2.955	2.962	2.970	2.976
.0024641-----	2.908	2.910	2.913	2.917	2.919	2.924	2.928	2.933	2.940	2.946	2.954	2.962	2.971
.0031025-----	2.871	2.870	2.873	2.876	2.880	2.883	2.887	2.894	2.900	2.908	2.914	2.923	2.931
.0036743-----	2.840	2.842	2.844	2.848	2.852	2.856	2.860	2.866	2.874	2.881	2.889	2.897	2.906
.0050000-----	2.792	2.794	2.797	2.801	2.805	2.809	2.814	2.823	2.828	2.835	2.843	2.852	2.864
.0071782-----	2.745	2.745	2.747	2.750	2.754	2.759	2.764	2.773	2.780	2.788	2.796	2.806	2.816
.0090000-----	2.714	2.716	2.718	2.722	2.726	2.731	2.738	2.747	2.752	2.759	2.769	2.779	2.790



TABLE 15.—pH values of aqueous mixtures of acid potassium phthalate and *o*-phthalic acid containing various amounts of potassium chloride from 0° to 60° C

SERIES III. MOLALITY OF <i>o</i> -PHTHALIC ACID=MOLALITY OF ACID POTASSIUM PHTHALATE=0.018													
Molality of potassium chloride	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
<i>Moles of solute per 1,000 g of water</i>													
0.005.....	2.921	2.923	2.926	2.931	2.935	2.941	2.948	2.955	2.964	2.974	2.983	2.992	3.007
.008.....	2.919	2.920	2.924	2.928	2.933	2.939	2.946	2.953	2.961	2.971	2.982	2.992	3.005
.010.....	2.916	2.918	2.920	2.926	2.928	2.937	2.943	2.950	2.959	2.968	2.979	2.989	3.004
.014.....	2.914	2.916	2.920	2.925	2.929	2.935	2.942	2.949	2.957	2.966	2.977	2.989	3.001
.018.....	2.910	2.912	2.918	2.919	2.924	2.932	2.936	2.944	2.953	2.962	2.973	2.984	2.998

TABLE 16.—pH values of aqueous mixtures of acid potassium phthalate and *o*-phthalic acid containing various amounts of potassium chloride from 0° to 60° C

SERIES IV. $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID}=0.018 \\ \text{MOLALITY OF ACID POTASSIUM PHTHALATE}=0.009 \end{array} \right.$													
Molality of potassium chloride	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
<i>Moles of solute per 1,000 g of water</i>													
0.03000.....	2.718	2.721	2.723	2.726	2.731	2.736	2.741	2.749	2.756	2.765	2.773	2.785	2.796
.05000.....	2.717	2.719	2.721	2.724	2.730	2.734	2.740	2.748	2.755	2.763	2.773	2.783	2.793
.06985.....	2.716	2.717	2.720	2.723	2.728	2.733	2.739	2.746	2.754	2.761	2.771	2.782	2.792
.09000.....	2.714	2.715	2.718	2.721	2.725	2.731	2.736	2.744	2.753	2.759	2.768	2.779	2.790
.04931.....	2.699	2.700	2.703	2.707	2.711	2.718	2.721	2.726	2.734	2.747	2.751	2.760	2.770

TABLE 17.—pH values of aqueous mixtures of acid potassium phthalate, *o*-phthalic acid and potassium chloride from 0° to 60° C

SERIES V. $\left\{ \begin{array}{l} \text{MOLALITY OF } o\text{-PHTHALIC ACID}=1.5 \times \text{MOLALITY OF ACID POTASSIUM PHTHALATE} \\ \text{MOLALITY OF POTASSIUM CHLORIDE}=1.5 \times \text{MOLALITY} \end{array} \right.$													
Molality of acid potassium phthalate	Temperature in degrees centigrade												
	0	5	10	15	20	25	30	35	40	45	50	55	60
<i>Moles of solute per 1,000 g of water</i>													
0.009423.....	3.210	3.211	3.213	3.214	3.217	3.220	3.225	3.229	3.234	3.289	3.245	3.252	3.258
.0016280.....	3.090	3.090	3.091	3.094	3.098	3.101	3.105	3.112	3.117	3.121	3.130	3.137	3.145
.0026071.....	3.001	3.002	3.004	3.008	3.011	3.104	3.020	3.025	3.031	3.039	3.043	3.053	3.063
.0030788.....	2.972	2.973	2.976	2.979	2.982	2.986	2.991	2.998	3.003	3.011	3.017	3.027	3.037
.0036444.....	2.942	2.943	2.946	2.950	2.954	2.957	2.963	2.971	2.977	2.983	2.992	3.001	3.010
.0038552.....	2.934	2.935	2.938	2.942	2.945	2.948	2.956	2.961	2.967	2.975	2.982	2.992	3.000
.0041264.....	2.923	2.925	2.927	2.930	2.934	2.938	2.944	2.950	2.956	2.964	2.973	2.981	2.991
.0044082.....	2.913	2.913	2.917	2.921	2.924	2.929	2.934	2.941	2.948	2.956	2.963	2.972	2.982
.0054960.....	2.881	2.885	2.887	2.891	2.894	2.898	2.905	2.911	2.919	2.925	2.935	2.945	2.954
*.0056467.....	2.875	2.879	2.881	2.884	2.888	2.894	2.898	2.904	2.912	2.919	2.928	2.938	2.948

In figure 6 a few of the values of series I (table 13) are shown plotted as a function of the temperature. The curves for different molalities are almost parallel. The data of the other tables give similar plots.

The values in tables 14 and 15 give the effect of potassium chloride on the pH of solutions containing mixtures of *o*-phthalic acid and acid potassium phthalate. The magnitude of the effect is very small. The pH values for any solution of *o*-phthalic acid potassium phthalate

in the ratio from 2 to 1, with or without potassium chloride, may be interpolated from large-scale plots of the data of tables 13 to 17 with respect to the concentration of acid potassium phthalate.

Each solution may be used as a pH standard. It is proposed that they be prepared either from the NBS Standard Sample of acid potassium phthalate and standardized hydrochloric acid, or from acid potassium phthalate, recrystallized potassium chloride, recrystallized *o*-phthalic acid prepared from resublimed phthalic anhydride, and distilled water of pH 6.7 to 7.3 having a specific conductance not over  $1.0 \times 10^{-6}$  mho. The solutions may be used to calibrate a variety of pH equipment. Solutions of higher concentrations than those reported in this investigation should not be employed in the preparation of pH standards. If so, crystals of phthalic acid will separate out if the temperature falls much below 25° C.

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